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# **FINAL REPORT, 2004**

## **MOLECULAR PHOTODYNAMICS IN SUPERFLUID HE**

**AFOSR Grant F49620-01-1-0083**

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### **Introduction**

A rather fruitful investigation of photodynamics in superfluid helium was accomplished under the AFOSR grant. We carried out *the first real-time measurements* of molecular dynamics in superfluid helium, and we introduced *the first method for simulations of dynamics* (all other methods aim at calculating stationary eigenstates). Moreover, in a rather satisfying manner we addressed the principal question that we had set out to investigate, namely, the scaling of concepts of superfluidity to the molecular length and time scales. This was accomplished by the combination of ultrafast time-resolved measurements, high level ab initio theory to develop effective potentials, and the development of time-dependent density functionals to simulate the observables and to test out the predictions of two-fluid hydrodynamics which was originally developed to treat macroscopic phenomenology in superfluid helium.

### **Accomplished Science**

In the first of our publications in this field, we demonstrated the use of strong-fields in superfluid helium to generate Rydberg states which lie above 18 eV [1]. The experiments allowed the detailed description of strong-field induced ionization, localization of charges, formation of electron bubbles, and their diffusion controlled recombination. With a nonparametric theory, we were able to reproduce all observables – photocurrent, ion yield, laser-induced fluorescence as a function of intensity and time – to develop one of the most complete descriptions of strong field ionization and dielectric breakdown in the condensed phase [1]. An important follow-up to this work was to demonstrate the contrast between He and Xe, by carrying out strong field ionization experiments in liquid Xe (breakdown is completely inhibited in Xe due to defocusing of the beam through plasma induced cubic susceptibility) [2]. With the method for sudden generation of Rydberg states developed, we carried out time dependent measurements of the liquid response to Rydberg excitations [3]. The measurement is best understood as that of an Å-scale viscosimeter, which measures the damping of spherical waves generated by sudden expansion of the electron cloud on a molecular center. The observed damped dynamics could be treated using two-fluid hydrodynamics – a result, which in itself, was a significant finding. To test the validity of such a treatment we developed the time-dependent density functionals approach as a numerically intensive, however rigorously accurate treatment of dynamics, and now compared the predictions of

continuum hydrodynamics with the quantum treatment of the well-established electron-bubble problem [4]. This work rigorously showed the scalability of the hydrodynamic equations, and in addition, clearly showed that the results of real-time measurements are extremely sensitive to details of the potentials at long-range. Given the very low temperature of the medium, dynamics at very low energies are involved, as such potentials with accuracy of  $10^{-1}$ - $10^{-2}$  cm $^{-1}$  are needed for quantitative reproduction of the observables. This was of course the motivation in generating accurate Rydberg state potentials [5], which were used to interpret all of the known spectroscopy of Rydberg states in superfluid helium [6].

In addition to the above, we also worked on several different approaches to injecting molecules in the bulk liquid. Of these, the hot wire method was one that was demonstrated to work in principle, but not in a practically useful way to be applied. In parallel we developed the cryogenic pulsed-nozzle with laser driven ablation to dope [7]. This method produces micron-size droplets that are efficiently doped, and have as such been emulated and used by others in pulsed laser spectroscopy. We have since advanced the technique to develop a continuous fountain, which we plan to describe in the literature in the near future.

### **Human Resources**

The initial work on the time-resolved measurements in superfluid helium was carried out by postdocs: **Alexander Benderskii** and **Ruben Zadoyan**. Benderskii, has since assumed the position of Professor of Chemistry at Wayne State University; while Zadoyan, is at present the Senior Scientist at Intralase (developer of ultrafast lasers for eye-surgery). The theoretical work was principally carried out by **Jussi Eloranta**, who has since assumed the position of Professor of Theoretical Chemistry at the University of Jyvaskyla in Finland. The developments of helium injectors is carried out by a graduate student, **Vahan Ghazarian**, who continues to perfect the fountain source. The work on liquid Xenon was principally carried out by **Mika Petterson**, who presently is a fellow of the Science Academy in Finland, heading his own experimental group in ultrafast studies in condensed phase. N. Schwentner, Prof. of Physics from the Free University of Berlin has spent two summer sabbaticals with us, during which time he has made contributions to both experiments and interpretations. His name appears as co-author on many of our publications on helium.

### Cited Publications Resulting from the Grant

- (1) Benderskii, A. V., Zadoyan, R., Schwentner, N., and Apkarian, V. A., *J. Chem. Phys.*, 110, 1542 (1999). "Photodynamics in superfluid helium: Femtosecond laser-induced ionization, charge recombination, and preparation of molecular Rydberg states"
- (2) Pettersson, M., Zadoyan, R., Eloranta, J., Schwentner, N., and Apkarian, V. A., *J. Phys. Chem.* 106, 8308 (2002). "Strong-field excitation of liquid and solid Xe using intense femtosecond pulses"
- (3) Benderskii, A. V., Eloranta, J., Zadoyan, R., and Apkarian, V. A., *J. Chem. Phys.*, 117, 1201 (2002) "A Direct Interrogation of Superfluidity on Molecular Scales"
- (4) Eloranta, J., and Apkarian, V. A., *J. Chem. Phys.* 117, 10139 (2002). "A Time dependent density functional treatment of superfluid dynamics: Equilibration of the electron bubble in superfluid  $^4\text{He}$ "
- (5) Eloranta, J., and Apkarian, V. A., *J. Chem. Phys.* 115, 752 (2001). "The triplet  $\text{He}_2^*$  Rydberg states and their interaction potentials with ground state He atoms"
- (6) Eloranta, J., Schwentner, N., Apkarian V. A., *J. Chem. Phys.* 116, 4039 (2002). "Structure and Dynamics of  $\text{He}_2^*$  Bubble-States in Superfluid  $^4\text{He}$ "
- (7) Ghazarian, V., Eloranta, J., and Apkarian, V. A., *Rev. Sci. Instrum.* 73, 3606 (2002) "Toward a Universal Molecule Injector in Liquid Helium: Pulsed Cryogenic Doped Helium Droplet Source"